# SG and SSR approach in the preparation of precursors and influence on superconducting properties of Tl-1223 superconductors

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# Abstract

The paper presents the comparative analysis of the Sol-gel (SG) and solid-state reaction (SSR) route for the synthesis of precursors for thallium-based superconductors. Samples were prepared a two-step method and by sealed quartz tube technique in ambient pressure. Heat treatments of precursors showed that to obtain high-purity precursors, without any carbonate contamination for SG methods is sufficient to heat treatments at 915$^{o}$C temperatures and for SSR methods 945$^{o}$C. The diamagnetic onset temperature of the superconducting transition for the $TlBa_2Ca_2Cu_3O_{8+\delta}$ samples prepared by precursors SG at 915$^{o}$C and SSR at 945$^{o}$C is about T = 120 K and full screening of applied *ac* magnetic fields observed at T ≈ 102 K and T ≈ 94 K, respectively. The value of $J_c$ transport critical current densities for SSR obtained 128 A/cm$^2$, whereas for the SG sample and exactly 174 A/cm$^2$. We could conclude that the, using the wet chemistry offers some advantages in comparison with the classical solid-state ceramics processing, especially, better chemical homogeneity and higher reactivity of the precursor powder.


# 1 Introduction

Thallium-and mercury-based superconductors are generating considerable interest, as these systems set records for the transition temperature to the superconducting state. The Tl-1223 and Hg-1223 had the transition temperatures $T_c$≈115K and $T_c$≈133K when they prepared at ambient conditions. And when they synthesized under high pressures, the critical temperature can reach 133.5 K and 164 K, respectively [1–4]. The formula unit and crystal structure of the $TlBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ system similar to that of the $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ system, where (*n*) is the number of adjacent Cu-O layers. Mercury- and thallium are very toxic, volatile at high temperature, and what is more important for this family, to achieve high purity superconductivity phase, critically depends on the used precursor and synthesis conditions. Preparation of high purity and reaction ability precursor, in the various articles, was solved by diverse methods [5–11].

S.L. Loureiro et al. investigated importance [5] of average copper valence in the precursor for synthesized homologous series of Hg-1223 superconductors under high pressure. Have to note that, so that avoid problems elimination residual carbonate in the precursor, therefore in work, calcium oxide and barium nitrates were used as starting materials. A precursor was prepared by solid-state reaction methods. They show that average copper valence is a crucial dependence on the oxygen intake of non-stoichiometric phases during the precursor synthesis at a specific temperature, time, and cooling process treatment. By S. Lee and coauthors [6] proposed a method of freeze-dried for synthesized highly homogeneous precursors. For starting, materials have used nitrates. As a result, for Hg-1223 samples prepared from freeze-dried precursor were obtained 75% of Hg-1223 superconducting fazes and $T_c$ ~133 K. Metal-organic chemical vapor deposition methods are presented in articles [7, 8]. Precursor films have derived by employ $Ba(hfa)_2$mep, $Ca(hfa)_2$tet, $Cu(dpm)_2$ as metal sources. In this case, for the final synthesis necessarily need Thallium Fluorine for nucleating the Tl-1223 phase. In results were obtained high transport properties samples, with very short transition temperature. Sin et al. [9] have studied

simultaneously the influence of the Rhenium addition and in-situ gelation process using acrylamide monomers on the synthesis of precursors. The authors conclude that the rhenium based precursor is much more stable against moisture and carbonation. The urea combustion method for synthesizing precursors is present by T.M. Mendonca and coauthors [10]. The results showed that the in urea samples observed the single phase 99% vol., of the Hg-1223 phase. Brylewski et al. [11] have been reporting about the sol-gel method for synthesized $Ba_2Ca_2Cu_3O_x$ precursors. The starting materials were used nitrates and nitrates tetrahydrate, and as complexing agent ethylenediaminetetraacetic acid. Subsequently, was observed 89.1% of the high volume fraction of the (Hg,Pb)-1223 phase, The authors think, that EDTA chelating agent may be a reason for this.

The subject of this work is to synthesize the precursors separately by a sol-gel and solid-state reaction methods and based on that the Tl-1223 superconductors. It is mast note that for both ways, for starting materials was used oxide and carbonate-containing materials. For sol-gel route was used poly(vinyl alcohol)/poly(vinyl acetate) as the complexing agent [12, 13]. We present a comparative analysis with the data of samples $TlBa_2Ca_2Cu_3O_{8+\delta}$ obtained by the SG and SSR approach. The characterization of the superconducting parameters has investigated by the x-ray diffraction, the FTIR analysis. The phase method was used to study the real parts $-4\pi\chi'$ of the linear susceptibility. Errors in determination of $\chi'$ at higher frequencies than 1 kHz do not exceed 1% when $-4\pi\chi > 0.1$. For $4\pi\chi < 0.1$ the errors are increased in proportional to diminishing the magnitude of susceptibility and frequency. For the measurements of intergranular critical current densities, we used the method of high harmonics. The error of measurement of high harmonics was approximately 2% when the measured signal was less than 0.2 μV and no more than 0.5% when the signal was higher. The measurements mainly performed at $h = 1$ Oe, $f = 20$ kHz, and $H = 0$. The Earth's magnetic fielded was shielded to less than $10^{-3}$ Oe by use of Permalloy screens [14–15].

# 2 Experimental

For synthesized $TlBa_2Ca_2Cu_3O_{8+\delta}$ samples, we used the two-step method. In the first stage, a Tl-free precursor has prepared before proceeding to the second stage, where $Tl_2O_3$ has added to the precursor before final sintering. We note that for both methods, starting materials have utilized powders materials $BaCO_3$ (99.0% Oxford Chem Serve), $CaCO_3$ (99.98% Oxford Chem Serve), CuO (99.999% Sigma-Aldrich) and $Tl_2O_3$ (99.99% Sigma-Aldrich).

Preparation of Ba:Ca:Cu = 2:2:3 multiphase ceramic precursors:

**Sol-gel method (SG)**. The initial reactants were dissolving separately, $BaCO_3$ and $CaCO_3$ in acetic acid and CuO in nitric acid. When the complete dissolution has achieved, all the solutions were mixed, and the poly(vinyl alcohol)/poly(vinyl acetate) $([\text{-}CH_2CHOH\text{-}]_n/[CH_2CH(O_2CCH3)]_n$, (Sigma-Aldrich) has added as the complexing agent. The solution was stirring slowly, with continuous up to 80°C, then obtained green gel was dried slowly, the temperature rate 1°C per minute up to 300°C. The result was a black powder that

was then grounded in an agate mortar. Then, the powdered was calcined at 900$^{o}$C in the air with a heating rate of 2$^{o}$C /min, for 12 h, with two intermediate grindings.

The resulting powders were ground, separated into six parts, and pressed in the form of a disc. For the eliminates the $CO_2$ from precursors, each pellet was individually annealed tube-type furnace at different temperatures 700$^{o}$C, 800$^{o}$C, 900$^{o}$C, 915$^{o}$C, 930$^{o}$C, and 945$^{o}$C in flowing oxygen partial pressure of 0.5 bar for 12 h. For all synthesis temperature heating rate was 1$^{o}$C/min. First, the samples heated until the temperature of the planned synthesis and then turned on the oxygen and keep on this temperature for 12 h. After the synthesized completed, we turned off the oxygen, and then samples cooled to room temperature inside the furnace.

**Solid-state reaction method (SSR)**. The materials $BaCO_3$, $CaCO_3$, and CuO were mixed in the stoichiometric ratio Ba:Ca:Cu = 2:2:3, and then they were ground carefully in an agate mortar. The resulting powder mixture was calcined in an alumina crucible in the air in a muffled furnace, with four time's intermediate grindings at 900 °C for 60 h. Then, as made above, the resulting powders also were separated into six parts, pressed and annealed under flowing $O_2$ in various temperatures.

In the second step both $Ba_2Ca_2Cu_3O_x$ precursors prepared by SG and SSR methods separately was mixed with $Tl_2O_3$ according to the composition $TlBa_2Ca_2Cu_3O_{8+\delta}$ and After final grinding the powder was pressed into a disc-shaped pellet 6 mm in diameter, and 3 mm thick, by using a hydraulic press under a pressure of 400 MPa. The samples have wrapped in a platinum foil then individually put into quartz tubes and from quartz tubes were evacuated up to $10^{-3}$ Torr and sealed. Thereafter, a quartz tube has inserted into a programmed muffle furnace. The temperature of the furnace was raised at a rate of 25$^{o}$C/min up to 900$^{o}$C and held at this temperature for 8 h. After the synthesis completed the furnace was quickly cooled to room temperature.

X-ray powder diffraction (XRD) patterns were obtained on a Dron-3 + PC diffractometer with CuKα radiation. The Fourier transformed IR of the samples was taken in the region 400–4000 $cm^{-1}$ on a Cary 600 series FTIR Spectrometer using the KBr disc technique. Scanning resolution 0.5 $sm^{-1}$. The samples were pulverized into a fine powder and then mixed with potassium bromide powder using a weight ratio of 1:100. The IR absorption spectra were measured immediately after preparing the discs.

# 3 Results And Discussion

As described above, to achieve the higher purity superconductivity phase critically depends on the used precursor. To get precursors with optimal properties best way is thermal annealing at the oxygen partial pressure, especially if precursors will be prepared from oxide containing carbonates. The synthesis of precursors in oxygen pressure provides the elimination of the carbonates in samples and the cation homogeneity and the oxygen content. The Absorption spectra of the precursors, with annealed in various temperatures, are shown in Fig. 1(a,b) for the range 400–4000 $cm^{-1}$. The signature of the $v_3$-triply

degenerated stretching mode of carbonate at ~1460 – 1360 $cm^{-1}$ is observed as SSR and for SG-precursors annealed at 700–900°C temperatures. The $v_2$-doubly degenerated stretching modes of carbonate (870 – 860 $cm^{-1}$) are observed only in precursors that have synthesized at 700°C and 800°C temperature [16–18]. By contrast, for SG-precursor annealed at 915°C remain $CO_3^{2-}$ impurity species are not observed and also for SSR-precursor annealed at 945°C.

The X-ray diffraction pattern of $Ba_2Ca_2Cu_3O_y$ precursor powder, prepared by the SG method at 800, 900°C and 915°C temperatures are plotted in Fig. 2 (a,b,c). As we see, in contrast, an IR results in XRD measurements $BaCO_3$ is fixed only at 800°C temperature. In samples annealed at 900°C and above, no carbonate $CO_3^{2-}$ is observed, as SG and for SSR precursors. A sample practically consists of only two phases of $BaCuO_2$ and $Ca_2CuO_3$ and only small amounts of $Ba_2Cu_3O_5$ and unreacted CaO phases identified. The High purity precursors were obtained for SG and SSR at 915°C and 945°C, respectively. The precursor consists of only two-phase of $BaCuO_2$ and $Ca_2CuO_3$ [19–21]. From XRD measurement results, we can conclude that the sensitivity of X-ray diffraction to fixing carbonate is not sufficient.

Figure 3 (a, b) presented to compare the XRD patterns of the superconducting samples with the nominal composition $TlBa_2Ca_2Cu_3O_y$, prepared on the best precursor powders of both methods: SSR synthesized at 945°C and SG synthesized at 915°C temperatures. From the XRD results, one will notice that small amounts of impurities such as Tl-1212 and $BaCuO_2$, which are usually present in the preparation of the Tl-1223 phase, have appeared. It can see that both prepared samples are nearly a single phase, has a tetragonal structure with the lattice parameters for SSR method $a$ = 3.846 (Å), $c$ = 15.908 (Å) and SG method $a$ = 3.847 (Å), $c$ = 15.920 (Å).

The temperature dependencies of the susceptibility versus temperature for the Tl-1223 samples prepared on the based precursors that are synthesized by SSR and SG methods are present in Fig. 4 (a,b). The samples synthesized with precursors prepared using the SSR method, which gated thermal treatments at a temperature 900°C, 915°C, 930°C, and 945°C diamagnetic onset are at Tc ≈ 114 K, 117 K, 118 K, and 120 K, respectively. The full diamagnetic state observed at $T_c$≈78 K (915°C), $T_c$≈88 K (930°C), and 92 K (945°C). Unlike from the SSR in the SG samples, the diamagnetic onset temperature of the superconducting transition for the SG samples synthesized at 900°C and 915°C are $T^c$≈117 K and 120 K, respectively. And the full diamagnetic state is $T_c$≈90 K and 102 K, respectively.

In Fig. 5 presented the variation dependence intergrain critical current density the Tl-1223 samples synthesizing with precursors prepared at various temperatures, as for SSR and SG methods. The value of $J_c$ at 78K for SSR (945°C) is little 128 $A/cm^2$ in comparison to the SG sample (915°C) and equal 174 $A/cm^2$. It is due to the fact, despite the transition temperature as for SSR (945°C) and for SG (915°C) is the same, full diamagnetic state is observed at 92K and 102K, respectively.

# Conclusion

We have reported the preparation of Tl-1223 high-temperature superconductors by sealed quartz tube technique. For the synthesis samples, we used the two-step method. In the first stage were prepared, multiphase precursors in the second stage where $Tl_2O_3$ added. Precursors synthesized by two methods, sol-gel, and solid-state reaction methods and examined the influence of heat treatment on precursors. These results showed that to obtain high-purity precursors for SG methods sufficiently heat treatments at 915$^oC$ temperatures and for SSR methods 945$^oC$. The diamagnetic onset temperature of the superconducting transition for the samples prepared by precursors SSR at 945$^oC$ and SG at 915$^oC$ is about T≈120 K and full diamagnetic state observed at T ≈ 92 K and T ≈ 102 K, respectively. The value of $J_c$ at 78K for SSR (945$^oC$) is 128 A/cm$^2$ in comparison to the SG (915$^oC$) sample and equal 174 A/cm$^2$. It is caused that, despite the transition temperature for both samples are the same, full diamagnetic state is observed at various temperatures. As a result, we could conclude that the SG method demonstrated as a successful alternative to the SSR method allowing a faster production of the precursors without any carbonate contamination.

## Declarations

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# Figures

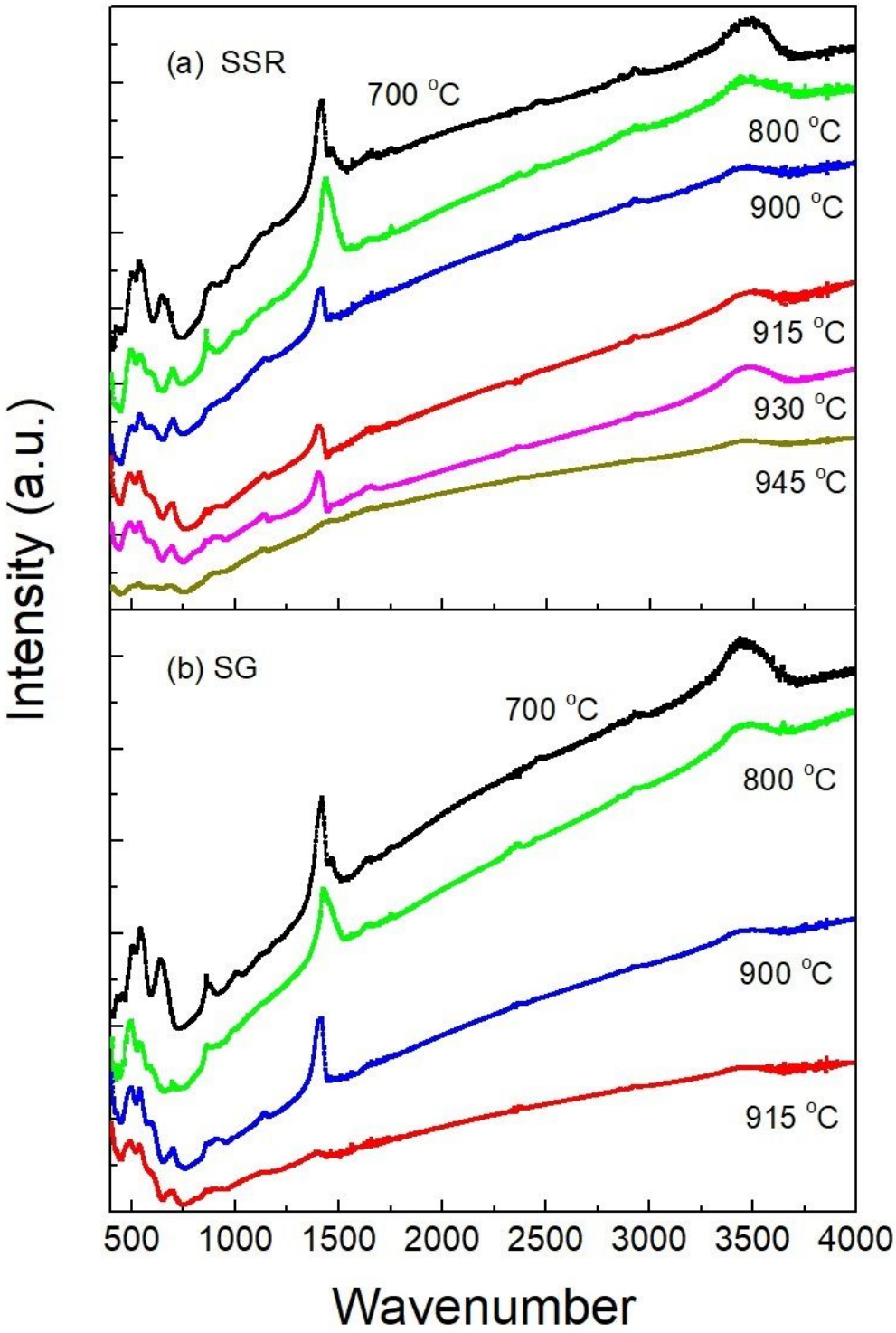


**Figure 1**

IR analysis of Ba2Ca2Cu3Oy after annealing in flowing oxygen partial pressure of 0.5 bar: for SSR-precursor at 700oC-945oC (b) and for SG-precursor at 700oC -915oC.

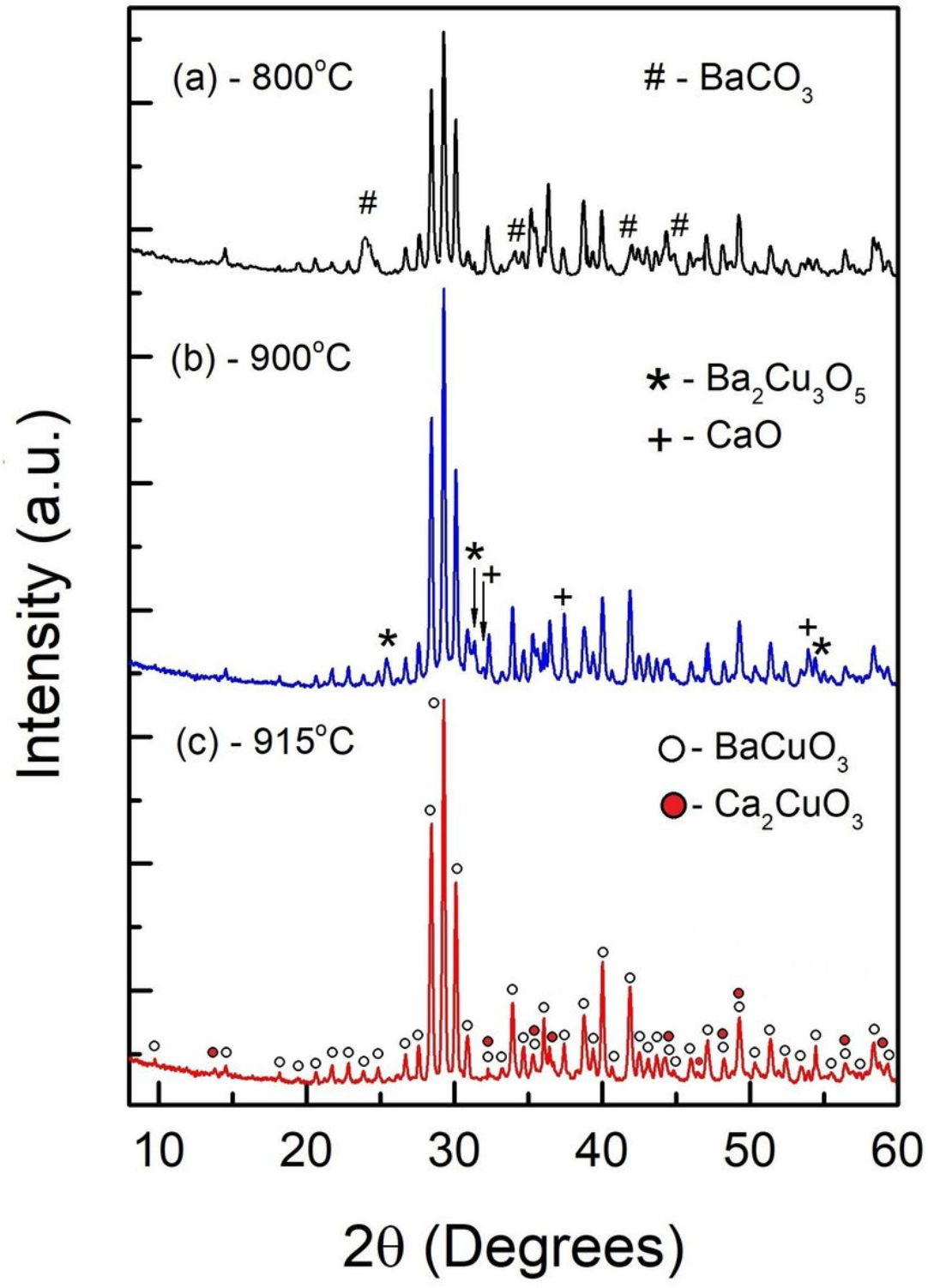


**Figure 2**

XRD patterns of the Ba2Ca2Cu3Oy precursor, prepared by the SG method at 800, 900°C and 915°C temperatures.

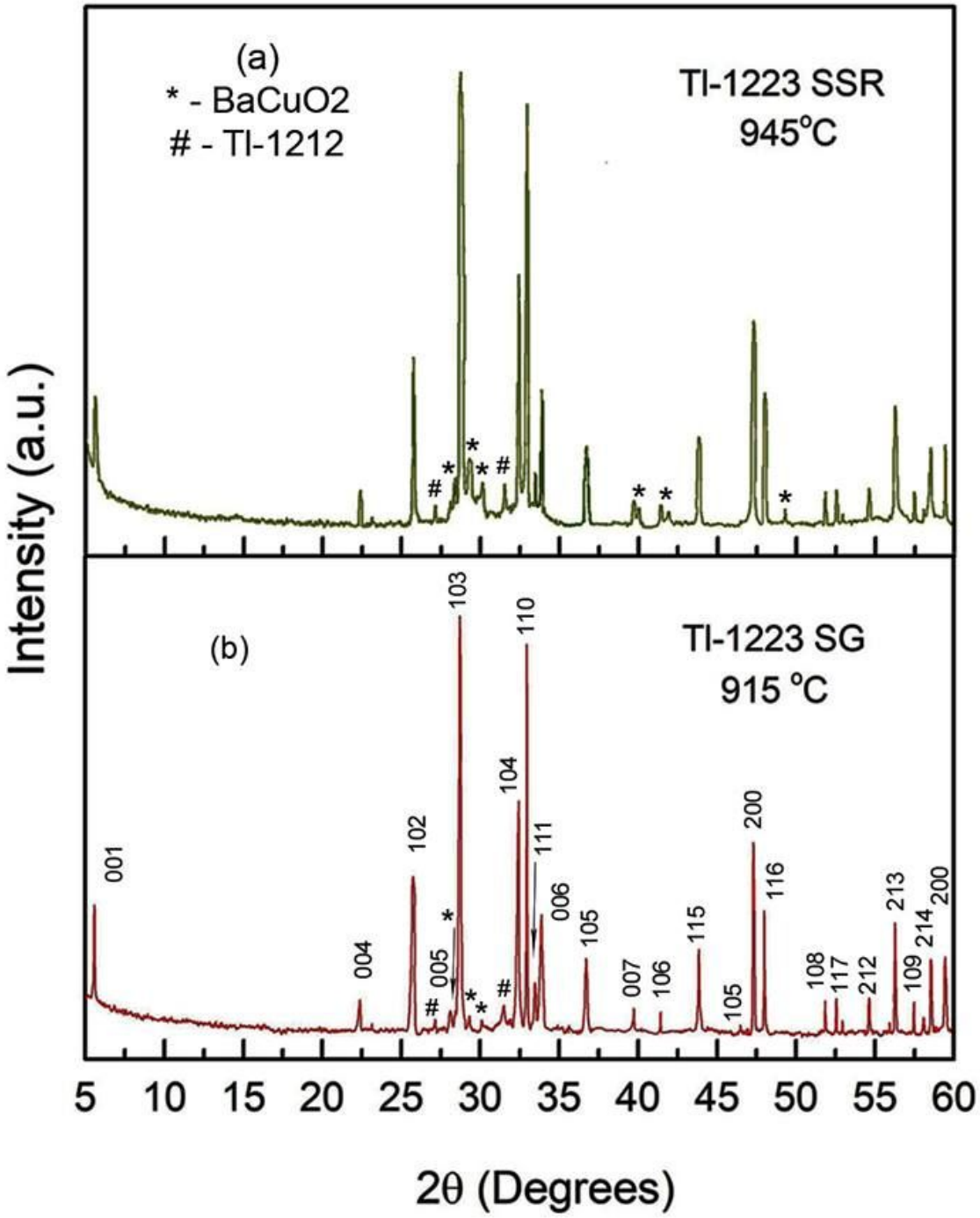


**Figure 3**

XRD patterns of the TlBa2Ca2Cu3O8+δ samples, prepared on the best precursor powders of both methods: (a) SSR synthesized at 945oC and (b) SG synthesized at 915oC temperatures.

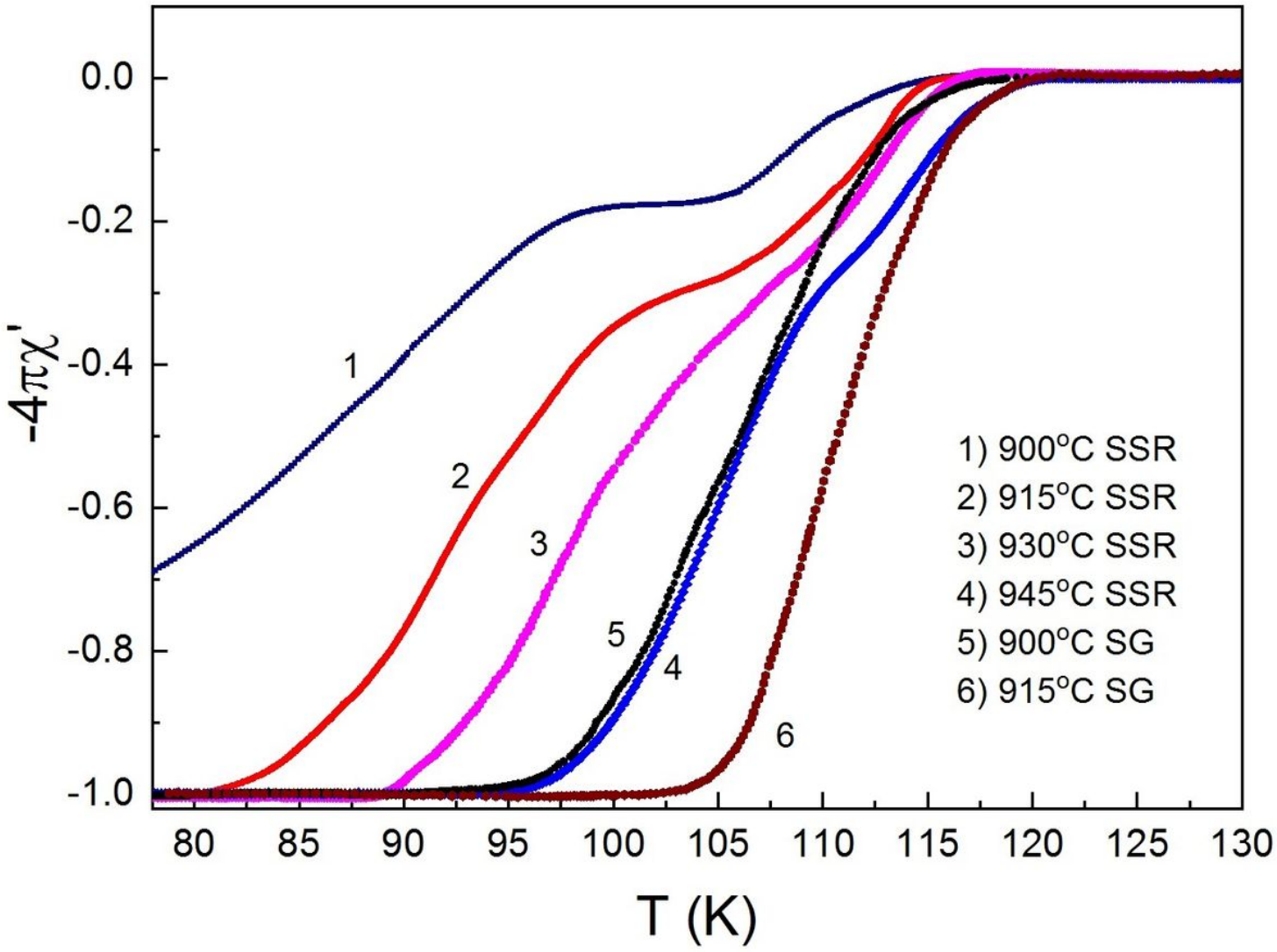


**Figure 4**

Temperature dependences of the real -4πχ' part of ac susceptibility for the SG and SSR samples.

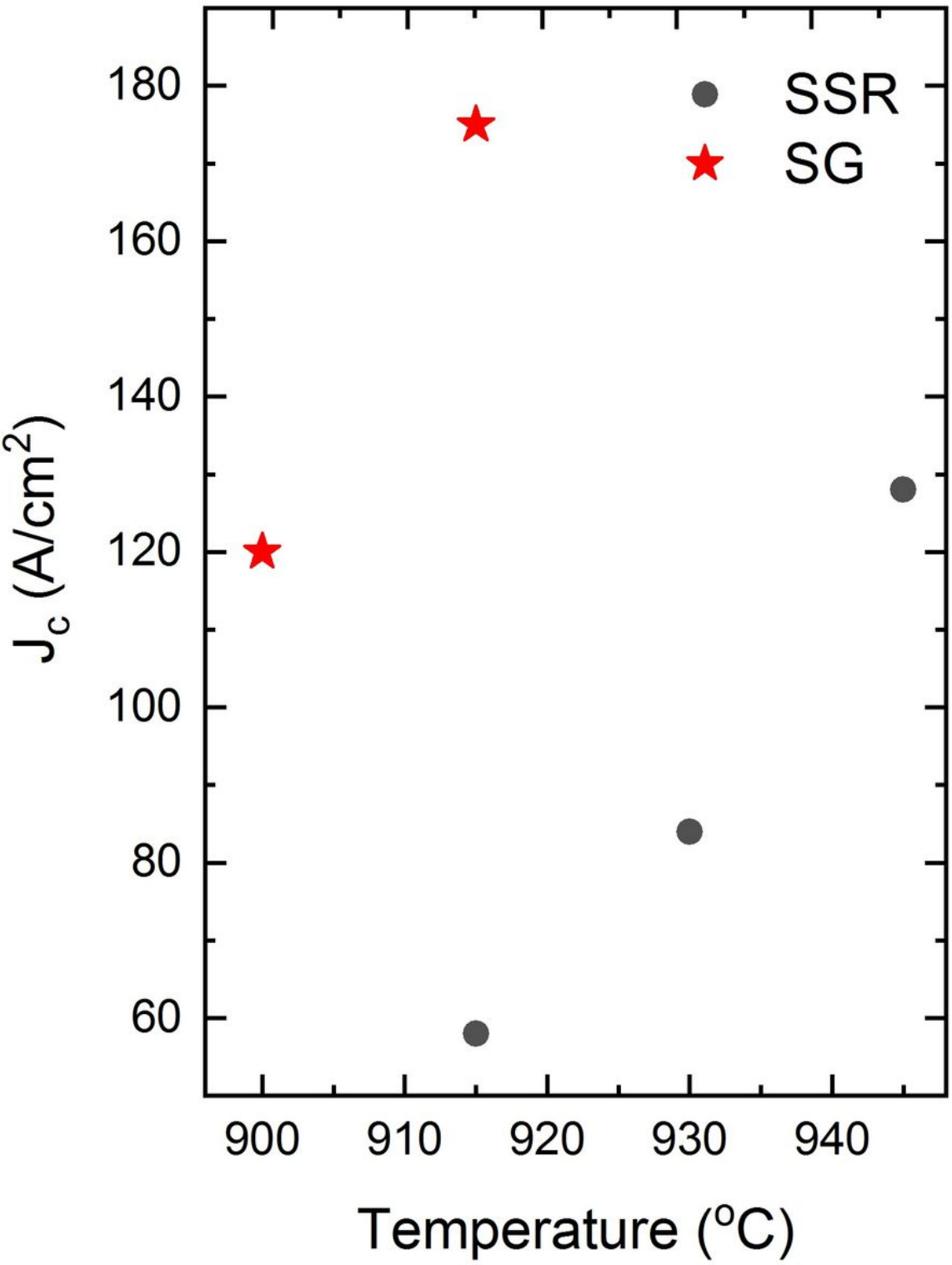


**Figure 5**

Dependencies of the Jc transport critical current densities versus precursor synthesis temperature, for the SSR and SG samples.